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Analysis of Priority Pollutants at a Primary Zinc Production Facility

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Results indicate high levels of zinc, cadmium, and chrome being generated but being removed to acceptable state requirements by the treatment plant. Low levels of several priority pollutant organics were found, originating either in the city water supply or being generated chemically within the manufacturing plant.

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ANALYSIS OF PRIORITY POLLUTANTS AT A PRIMARY ZINC PRODUCTION FACILITY

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FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory - Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

This report evaluates the removal efficiency of the 129 priority pollutants due to existing wastewater treatment technology at a single primary zinc plant. A brief process description and a detailed description of sampling, analytical, quality assurance, and treatment plant assessment are presented. Results of the investigation will enable EPA to identify which priority pollutants are being emitted by industry and to determine the ability of wastewater treatment technologies to remove priority pollutants. Questions or comments regarding this report should be addressed to the Metals and Inorganic Chemical Branch of the Industrial Environmental Research Laboratory in Cincinnati.

David G. Stephan
Director
Industrial Environmental Research Laboratory
Cincinnati

ABSTRACT

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SECTION 1

INTRODUCTION

On 7 June 1976, the U.S. District Court of Washington, D.C., issued a consent decree (resulting from Natural Resources Defense Council, et al v Train) requiring EPA to enhance development of effluent standards for 21 industrial point sources, including nonferrous metals manufacturing. Among other requirements, the court mandate focused federal water pollution control efforts on potentially toxic and hazardous chemical compounds. As a result, a list of 129 surrogate chemicals, known as priority pollutants, was established. The consent decree obligates EPA to identify which priority pollutants are present in industrial wastewaters and to determine the ability of various wastewater treatment technologies to remove priority pollutants.

Therefore, the objective of this project was to provide accurate data on the concentration of the 129 priority pollutants in wastewater samples collected from a single primary zinc plant equipped with a well designed wastewater treatment plant. In addition, the removal efficiency for priority pollutants was evaluated.

This report provides a brief process description and a detailed description of the sampling, analytical, and quality assurance procedures employed. Analytical results and evaluation of the treatment plant are then presented.

SECTION 2

SUMMARY

A primary zinc plant was sampled for the 129 priority pollutants from 8 March 1978 to 10 March 1978. The sampled plant produces on an average 189,000 kilograms of cathode zinc and 600 kilograms of cadmium per day. The plant operates 24 hours a day, 7 days per week utilizing both zinc sulfide and zinc oxide in producing high grade zinc and zinc alloys.

The plant treats all wastewater, both process and cooling, and rainfall runoff in a central physical/chemical waste treatment plant. The average wastewater flow treated per day is 2,540 kiloliters. Sources of wastewater to the treatment plant are gas scrubber wastewater from the roasting operation and holding lagoon wastewater. The lagoon collects all other plant generated wastewater including a sanitary discharge that has received primary treatment and chlorination.

Five locations in the plant were sampled for priority pollutants. These were:

- city water supply
- sanitary discharge
- gas scrubber wastewater
- lagoon wastewater
- plant effluent

Sampling techniques followed EPA protocol.

Results indicate low levels of several priority pollutant organics, either entering the plant in the city water supply or generated chemically within the plant. Metals analysis indicates high levels of zinc, cadmium, and lead, being generated but being removed to acceptable state requirements by the treatment plant. The plant operates effectively but is currently overloaded with solids. Net effluent factors for the plant discharge and metal removal efficiencies are presented in Tables 1 and 2.

TABLE 1. NET EFFLUENT FACTORS FOR SAMPLED ZINC PLANT

Total metal (AA)	Net effluent factor, mg/kg of zinc
Silver	0.10
Beryllium	-[a]
Cadmium	0.29 ± 0.05
Chromium	2.1 ± 0.1
Copper	0.14
Nickel	-[a]
Lead	-[a]
Antimony	-[a]
Zinc	11
Arsenic	-[a]
Mercury	-[a]
Thallium	-[a]
Selenium	0.6 ± 0.01

[a]Net effluent factor cannot be calculated since the metal concentration in both samples was below instrument detection limits.

TABLE 2. REMOVAL EFFICIENCIES FOR SAMPLED ZINC TREATMENT PLANT

Total metal (AA)	Removal efficiency, percent
Silver	94
Beryllium	-[a]
Cadmium	100
Chromium	93
Copper	100
Nickel	94
Lead	100
Antimony	-[a]
Zinc	100
Arsenic	99
Mercury	99
Thallium	-[a]
Selenium	85

[a]Removal efficiency cannot be calculated since the metal concentration in all samples was below instrument detection limits.

SECTION 3

SOURCE DESCRIPTION

GENERAL

The sampled plant produces special high grade electrolytic zinc, 99.99 percent pure, in two separate operating departments.

The sulfide department treats zinc sulfide (ZnS) concentrates from mines in Honduras and Nicaragua.

The oxide department produces zinc oxide (ZnO) fume from the company's lead smelter in Texas. Zinc fume from the company's Montana smelter is also deleaded at the plant's Texas lead smelter before being sent to the sampled plant for processing.

In general, the operation of the oxide plant is similar to that of the sulfide plant. The oxide plant was built as a separate operation, however, because the sulfide plant could not treat relatively large quantities of germanium contained in some of the fume being processed.

The oxide plant has a production capacity 50 percent greater than the sulfide plant, producing about 4,900 metric tons of zinc per month compared to about 3,269 metric tons per month produced by the sulfide plant. Total zinc production in 1977 was 69,000 metric tons or 5,750 metric tons per month. Thus, zinc production at the sampled plant in 1977 was 70.4 percent of capacity.

Process Description

A flow diagram of the zinc refining operations at the sampled plant is shown in Figure 1.

Zinc sulfide concentrates are first converted to zinc oxide calcine by roasting. The calcine is leached in spent electrolyte containing 15-20 percent sulfuric acid to form a zinc sulfate ($ZnSO_4$) solution containing copper, cadmium, and other impurities in addition to zinc. Remaining in the residue are lead, silver, gold, iron, and other insolubles. Each metric ton of calcine yields from 200 to 250 kilograms of residue.

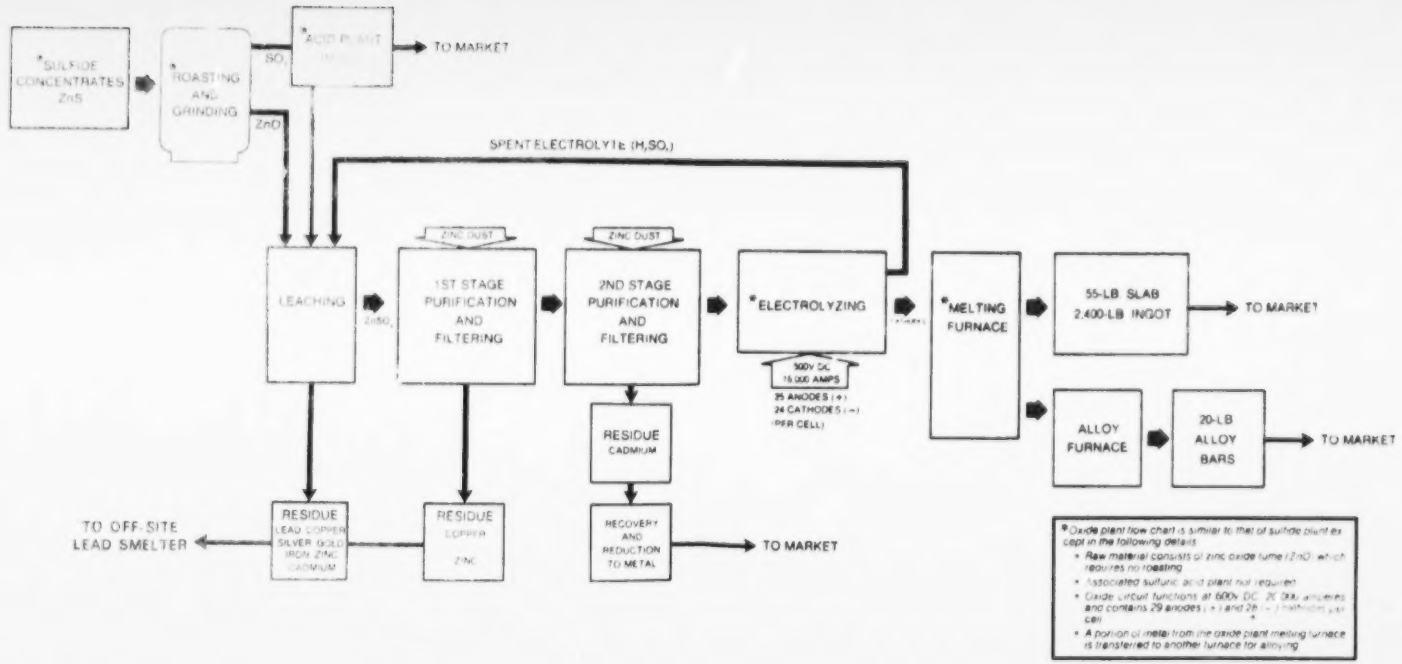

Figure 1. Zinc plant process flow diagram.

Most of the impurities in the solution (principally copper and cadmium) are precipitated in two purification stages using zinc dust as the cementing agent. Copper precipitates from the first purification are removed by filtration and sent to the Texas lead smelter for further treatment. Cadmium precipitates from the second purification stage are processed in the plant to produce the metal which is cast as balls and sticks.

In the electrolytic department, the purified zinc sulfate solution is added to a sulfuric acid-base electrolyte circulating through 280 of a total of 320 electrolytic cells. Responding to a charge of direct current, the zinc in solution plates out on the aluminum cathodes.

The zinc is stripped from the cathodes every 24 hours and charged into a reverbatory furnace for melting and casting into 25 kilogram slab and 1,090 kilogram ingot for market.

Zinc for the alloy melting furnace is taken molten from the melting furnace serving the oxide plant. Various percentages of magnesium, aluminum, copper, and nickel are added to the molten zinc to produce various high quality die alloys. The alloys are cast as 9 kilogram bars.

Plant produced zinc alloys are used principally in the manufacture of automobile grills, trim, and carburetor and fuel-pump housings. Large quantities are also used in household appliances, toys, and general hardware.

Zinc sulfate power, produced as a by-product, is made by drying purified zinc sulfate solution. It is used by the makers of insecticides and fertilizers and by the mining industry as a flotation reagent. The plant can produce 227 metric tons a month of this chemical. The yearly production capacity of this chemical is 2,724 metric tons.

Cadmium, also as a by-product, is removed as a precipitate in the second purification stage. Retreated, it is made into refined metal. It is sold to electroplaters for use in plating steel to protect it against rust and for use in surfacing bearings. Monthly capacity for cadmium metal is 27 metric tons. Total 1977 production of cadmium at this plant was 218 metric tons. Thus, cadmium production in 1977 at the sampled plant was 67 percent of total capacity.

Using sulfur dioxide from the roasting of sulfide ores, the plant produces up to 6,820 metric tons of sulfuric acid per month. A small amount is used as makeup in the leach process and the balance is sold. Total 1977 production of sulfuric acid at this plant was 59,474 metric tons. Thus, sulfuric acid production at the sampled plant was 73 percent of total capacity.

Water Usage

All water used in the sampled plant is bought and originates from the city water treatment plant. The water is taken from a freshwater surface supply by the city and softened with lime and a polyelectrolyte, filtered, and chlorinated before arriving by pipe at the zinc plant for in-plant uses. In 1977, the zinc plant purchased 1,406,377 kiloliters from the city. Based on this figure, the monthly average was 117,198 kiloliters, the daily average 3,853 kiloliters, and the hourly average 160 kiloliters. The plant operates 24 hours per day, 7 days per week.

The plant areas or operations using water and their estimated usage rates are shown in Table 3. The usage rates were estimated using plant supplied data for 1 February 1978 to 28 February 1978.

TABLE 3. MONTHLY WATER USAGE BY DIVISION FOR SAMPLED PLANT (FEBRUARY 1978)

Division	Water usage monthly total (kiloliters)	Daily average (kiloliters/day)
Waste-heat boilers	7,658	273
Process boilers	10,496	375
Roasting (cooling)	17,245	616
Laboratory	469	17
Change house (sanitary)	1,249	45
ZnS leaching	2,854	102
ZnO leaching	2,706	97
ZnS purification	2,078	74
ZnO purification	1,556	56
ZnS cell division	2,388	85
ZnO cell division	2,596	93
ZnS casting (contact cooling)	1,764	63
ZnO casting (contact cooling)	1,764	63
Pilot plant	466	17
Air compressor cooling	1,529	55
Demineralizer[a]	38,871	1,388
Zinc duct (mixing)	76	3
$ZnSO_4$ purification	223	8
ZnO die casting (contact cooling)	337	12
Cadmium (contact cooling)	337	12
Acid plant (scrubbing)	12,180	435
TOTALS:	108,892	3,889

[a]Does not include waste-heat and process boiler water which is also demineralized.

The major water demand in the zinc plant is for demineralized water. Of the 38,871 kiloliters per month demineralized (excluding boiler feed water), approximately 18,420 kiloliters is used as part of two scavenger processes in the purification areas. An additional 6,828 kiloliters per month is used as wash water in the leaching operations. The remaining 16,623 kiloliters per month is used for regeneration of the demineralizers and for dilution water in the production of sulfuric acid. The regeneration water requirements account for approximately 80 percent of this remaining 16,623 kiloliters per month.

Sources of Wastewater

All water used within the zinc plant is eventually treated by the plant's waste treatment system before being discharged to a surface waterway. This includes any rainwater runoff up to 12.7 centimeters of rain in 24 hours. The major exceptions to this are 1) demineralized water leaving as dilution water in plant produced surfuric acid (98 percent H_2SO_4), 2) demineralized water lost as steam from the plant boilers, 3) cooling tower drift and evaporation, 4) evaporation from the treatment plant holding lagoon, and 5) water leaving the waste treatment plant in sludge residues.

All wastewater, including rainfall runoff within the plant boundaries is sent to the treatment plant holding lagoon except for the gas scrubber wastewater from the roasting operation which enters the treatment plant in a separate pipe. This gas scrubber wastewater results from the scrubbing of the roaster smoke stream for particulate removal. The scrubber treats the smoke immediately after a Cottrell electrostatic precipitator system. During the sampling period, the gas scrubber wastewater flow averaged 170 liters per minute but on the previous month averaged 295 liters per minute. This waste stream travels to the treatment plant in polyvinyl chloride plastic pipe.

As mentioned, the holding lagoon collects all other wastewater generated within the zinc plant. The major source of wastewater is noncontact cooling water. All cooling water receives 5.7 liters of scale, corrosion, and foaming inhibitors, approximately 8.2 kilograms of chromate, and 8.2 kilograms of chlorine per day. Contact cooling water from zinc and cadmium casting also is sent to the holding pond. Noncontact cooling water is both used on a once-through (roasting) and closed loop (all other plant cooling) basis. Cooling tower blowdown and contact cooling flow rates to the holding lagoon are not measured by the plant and thus actual flow to the lagoon is not known.

Another source of wastewater to the holding lagoon is regenerate waste from the demineralizers. Again, actual flow to the lagoon is not measured and is thus unknown. Regenerates used are sulfuric acid and caustic.

Another source of wastewater is process water from the zinc oxide and zinc sulfide leaching, purification and electrolytic operations. Cell house washing and spent solution wastage (none under normal operating conditions) are two examples of wastewater sources from these operations. Again, actual flow to the lagoon is not measured and is unknown.

Sanitary wastewater from the change (shower) house and other plant buildings receives minimal primary treatment with clorination (1.4 kilograms per day) to a residual of 1.5 to 3.0 mg/ℓ combined chlorine before being sent to the holding lagoon. An overflow wier allowed a measurement of flow during the sampling period for this source. Flow varied from 110 to 276 liters per minute and average 227 liters per minute.

As mentioned previously, all plant rainwater runoff is also sent to the lagoon. No rain was experienced during the sampling period and no runoff entered the lagoon.

Two minor sources of wastewater to the holding lagoon come from plant laboratory and pilot plant activities.

Wastewater Treatment Plant

The sampled plant has a physical/chemical waste treatment plant as shown in Figure 2. Wastewater enters the system from two sources. These are the gas scrubber and the holding lagoon. The holding lagoon has a design capacity of 22,710 kiloliters with a detention time of 7 days. Due to solids accumulation for which the lagoon was not designed for, current actual capacity is estimated to be 40 to 50 percent of design. The reason for this situation is discussed in the results and conclusion section of this report.

Both sources of wastewater to the treatment plant first enter the flash mixing tank, where they are contacted with slaked lime. Although the plant does not measure lime usage on a day-by-day basis, the lime slaker (when running) ran at 100 percent of the design rate of 11.35 kilograms per minute as CaO during the sampling period. The flash mixer has a 28 kiloliter capacity. Diffused air is also pumped into the mixer for agitation and mixing enhancement. The limed wastewater next enters the reactor clarifier. Immediately before entering the clarification section, a flocculant is added to aid in flocculation. Again, the plant does not measure an addition rate but daily usage amounted to approximately 22.7 kilograms. The clarifier, itself, is radial feed, central overflow in design. It has a capacity of 1,506 kiloliters, a design detention time of 6 hours, and a maximum design overflow rate of 3,936 liters per minute. During the sampling period, the clarifier had a clear depth (distance from water surface to sludge blanket) of 0.5 to 0.9 meters. The clarified wastewater overflows the clarifier and is discharged to the channel.

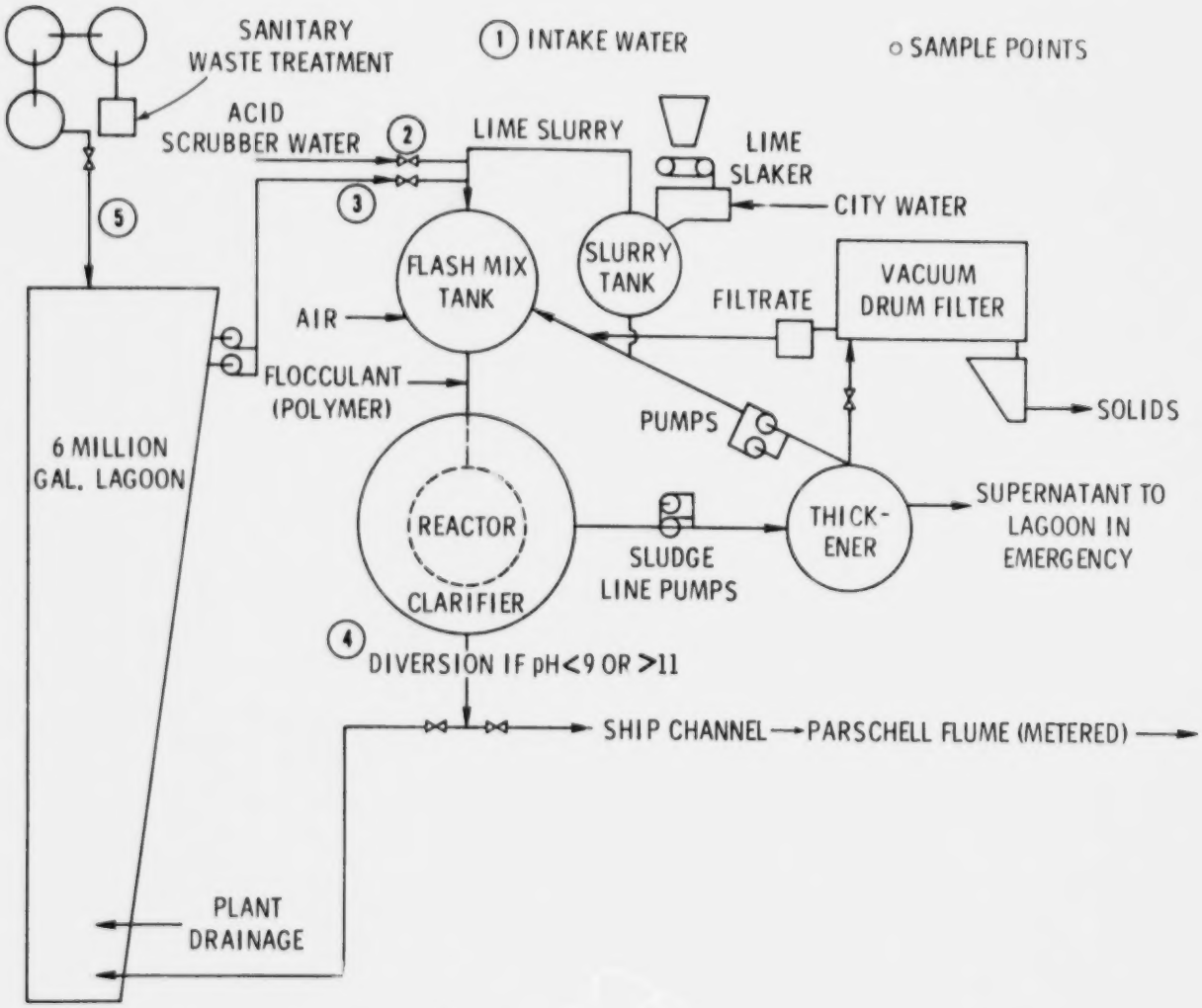

Figure 2. Zinc plant waste treatment system.

Effluent pH was in the 10-11 range during sampling but requires no adjustment due to applicable state standards for pH.

Solids leave the bottom of the clarifier and are pumped to a sludge thickener. Supernatant (overflow) off the thickener was designed to be discharged to the flash mixing tank but is currently recycled back to the lagoon. The thickener has a 174 kiloliter capacity, detention time of 10-11 hours, and design overflow rate of 102 liters per minute. Thickened solids (5-10 percent by volume) are pumped from the thickener bottom to a vacuum filter. Filtrate off the vacuum filter was designed to flow to the thickener at a rate of 45 liters per minute but currently is sent to the flash mixer. Filter cake (15 to 30 percent solids by volume) is pumped to drying beds on the plant site. Dried solids are shipped to a registered solid waste disposal site, for an annual fee paid by the plant.

During the sampling period (48 hours), the treatment plant discharged 5,800 kiloliters or 2,900 kiloliters per day. During 1977, the treatment plant discharged 927,000 kiloliters or 2,500 kiloliters per day. Allowing for scheduled maintenance and other down time during 1977, the amount of wastewater treated during the sampling period is considered representative of normal plant operation.

SECTION 4

SAMPLING AND ANALYSIS PROTOCOL

SAMPLING PROCEDURE

Collection Technique

Wastewater sample collection techniques followed those recommended by EPA in Reference 1, with a few modifications designed to better insure sample integrity, chain of custody, and site specific requirements. Since the plant operated 24-hours/day, 7 days/week, 48-hour flow-proportioned samples were collected at the following locations:

- City water supply at the waste treatment plant laboratory sink,
- holding lagoon water approximately 15 meters from where it enters the waste treatment plant flash mixing tank,
- gas scrubber wastewater approximately 1.5 meters from where it enters the waste treatment plant flash mixing tank, and
- plant effluent approximately 18 meters downstream from the waste treatment plant reactor clarifier.

All four points were composited over a 48-hour period, from 10:00 A.M. March 8 to 10:00 A.M. March 10, 1978. The city water supply was the only sample point not flow proportioned.

Because of the way the wastewater treatment system was constructed (pressurized pipe flow), it was not possible to use automatic samplers and still guarantee sample integrity. Therefore, 48-hour grab samples were collected once every hour with a 11.3 liter Teflon®-lined stainless steel bucket. Aliquots were removed from the bucket using glass beakers and placed in the appropriate sample containers. Care was always taken to insure the sample remained homogeneous while in the bucket. It took

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(1) Draft Final Report: Sampling and Analysis Procedures for Screening of Industrial Effluents for Priority Pollutants. U.S. Environmental Protection Agency, Cincinnati, Ohio, April 1977. 145 pp.

approximately 5 minutes to remove all aliquots from the bucket and place them in the containers. For flow proportioning, the flow was first checked each hour, the bucket filled, and the appropriate volumes measured out.

A fifth sampling location was added on the second day of the 48-hour sampling period. After discussions with plant personnel, it was decided to run a 24-hour composite on the sanitary treatment plant effluent before it enters the holding lagoon. Due to both minimal soluble organics removal in the sanitary treatment plant and the addition of chlorine to the waste stream, it was felt that sufficient potential for trihalomethane formation existed to warrant an individual sample of this stream. Thus for a 24-hour period, samples were composited on a flow-proportioned basis in the same manner as the previously described four points.

Sampling logistics for subsequent priority pollutant analysis are shown in Table 4 (1, 2). Before sampling began, bottle labels were filled out and affixed to appropriate sample bottles. Figure 3 shows the bottle label designed by MRC for sample identification. Once applied to the bottle, clear tape was put over the label to prevent water damage to the label.

TABLE 4. SAMPLING LOGISTICS FOR PRIORITY POLLUTANTS

Analysis fraction	Container, per sampling point	Preservatives required (1, 2)
Volatile organics	4-40 ml glass vials w/Teflon-lined septa	Keep at 4°C, if residual chlorine is present (KI paper turns blue) then add 0.03 ml of 10% sodium thiosulfate to each bottle.
Nonvolatile organics (base/neutral, acid, pesticide, and PCB's)	1-3.785 liter amber glass pharmaceutical jug w/ Teflon-lined cap	Keep at 4°C.
Metals	1-500 ml plastic	In the lab add 5 ml of redistilled HNO_3, keep at 4°C.
Cyanide (total)	1-500 ml plastic	Adjust pH $\geq$ 12 w/10N NaOH, keet at 4°C.
Phenol (total)	1-500 ml glass	0.5 g $CuSO_4$ at beginning, adjust pH $\leq$ 4 w/H_3PO_4 (100 ml con H_3PO_4 to 1 liter of water) keep at 4°C.
Asbestos	1-1 liter plastic	1.0 ml of HgCl solution (2.71 g HgCl in 100 ml distilled water), keep at 4°C.

(2) Manual of Methods for Chemical Analysis of Water and Wastes. EPA-625/6-76-003a (PB 259 973). U.S. Environmental Protection Agency, Cincinnati, Ohio, 1976. 317 pp.

Job _____

Sample or Run No. _____

Sample Location _____

Type of Sample _____

Analyze for _____

Preservation _____

Comments _____

_____

_____

_____

Log No. _____ Date _____

Initials _____

Figure 3. MRC sample bottle label design.

Four samples, collected every twelve hours, were collected for volatile organics analysis, as opposed to the one grab sample recommended in Reference 1. Each of the four samples per stream were immediately hermetically sealed after collection and placed in ice at 4°C and were laboratory composited for one analysis per wastewater stream. Since there was no free chlorine, tested by potassium iodide paper, in any of the wastewater streams, preservatives were not required in the volatile organic sample (1).[a]

The time for volatile organic sample collection was as follows:

- 48-hour (lagoon, scrubber, city water, effluent) - 12:00 A.M. 8 March, 12:00 P.M. 8 March, 12:00 A.M. 9 March, and 12:00 P.M. 9 March.

- 24-hour (sanitary) - 4:00 P.M. 9 March, 12:00 P.M. 9 March, and 8:00 A.M. 9 March.

The grab sampling technique had the added advantage of field compositing samples for total cyanide and total phenol analyses as opposed to the one grab sample method described in Reference 1. Proper preservatives were added to these bottle in the beginning and proper preservation pH maintained throughout the 48-hour sampling period.

Asbestos samples were collected, preserved, and stored at 4°C for possible future analysis.

The pH of each sampling point was noted each hour from either automatic monitors or treatment plant operator measurements. The pH of the sanitary treatment plant discharge was not taken.

The temperature of the discharge from the zinc treatment plant was recorded hourly from an automatic monitor.

The flow of the gas scrubber waste stream and the plant discharge was recorded hourly from an automatic monitor. The flow of the holding lagoon waste stream was estimated for flow proportioning needs by difference between the treatment plant discharge flow and the gas scrubber waste stream flow. The sanitary treatment plant discharge flow was recorded hourly by measuring a 60° V-notched overflow wier. City water flow was not measured.

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[a]The city water supply and sanitary wastewater should have tested positive for free chlorine but did not. Free residual in the city supply had evidently dissipated by the time it reached the tap and the sanitary discharge was evidently very high in chlorine demand.

Sample Container Preparation

All glass containers and beakers were thoroughly cleaned with strong acid (50% sulfuric acid + 50 % nitric acid), rinsed in distilled water, and heated in a glass annealing oven at 400°C for at least 30 minutes. Once the bottles cooled to room temperature, Teflon-lined caps were applied.

Plastic bottles were thoroughly cleaned by washing in nitric acid and rinsing several times in distilled water.

During the first grab sampling period, each sample container was seasoned by rinsing with the appropriate wastewater sample and discarding the rinse.

Sample Shipping Procedure

At the completion of the 48-hour sampling period, all containers were checked to insure proper preservation. Then each bottle cap was taped to the bottle to prevent leakage during shipment. All glass bottles were wrapped with plastic glass packing material.

Sample containers were placed in plastic ice chests and filled with ice to maintain sample temperature at 4°C. Each ice chest was taped closed and appropriate shipping labels applied.

Samples were then taken to the airport and shipped via commercial air freight to Dayton for analysis. No sample containers were destroyed during transport to MRC.

Analytical Procedure

Recommended analytical procedures (1) developed by EPA were used throughout this project. It is important to realize that some of the procedures are still under development and require further verification and validation. Therefore, the data presented serve to identify which of the 129 priority pollutants (Appendix A) were present and to indicate the general concentration ranges within a factor of two.

Two of the 129 chemical species were not determined in this project: 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) and asbestos. EPA-Environmental Monitoring and Support Laboratory (EMSL) recommended that TCDD should be omitted because of its extreme toxicity and potential health hazard involved in preparing standard solutions in the laboratory from the pure compound (1). Asbestos samples were collected, preserved, and stored at 4°C for possible future analysis. Also, due to the source of wastewater in the primary zinc industry, pesticides were also not analyzed in the samples. The only source of pesticides would be the city water supply.

The analytical procedure (1) divides the 129 priority pollutants into six basic catagories: volatile organics, nonvolatile organics, metals, cyanide, phenol, and asbestos. Appendix B lists the chemical species which belong to each category. The following sections outline the analytical procedures and MRC modifications for analyzing each group of priority pollutants.

Volatile Organics

The recommended method for volatile organic analysis was designed by EPA to determine those chemical species which were amenable to the Bellar purge and trap method (1). Appendix B lists those priority pollutants classified as volatile organics.

Four hermatically sealed 40 ml glass vials collected from each of the five sampling points were composited in the laboratory for one analysis. Two composited solutions were used, one for analysis and one as a backup sample. Figure 4 is a simplified diagram of the analytical scheme for volatile organics analysis.

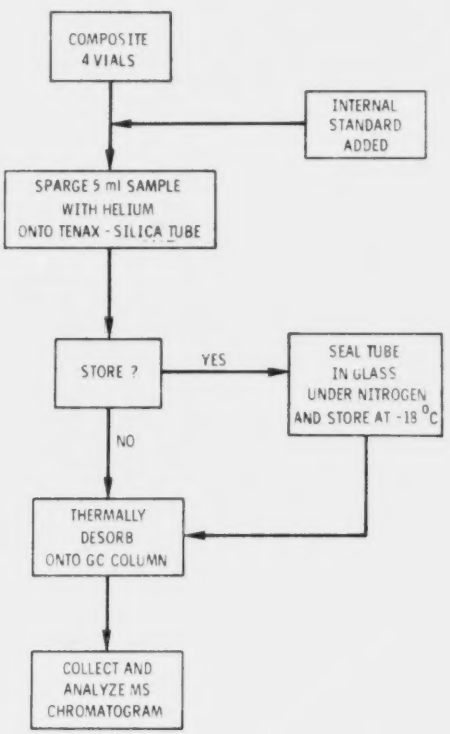
COMPOSITE 4 VIALS
INTERNAL STANDARD ADDED
SPARGE 5 ml SAMPLE WITH HELIUM ONTO TENAX - SILICA TUBE
STORE ?
YES
SEAL TUBE IN GLASS UNDER NITROGEN AND STORE AT -18 °C
NO
THERMALLY DESORB ONTO GC COLUMN
COLLECT AND ANALYZE MS CHROMATOGRAM

Figure 4. Analytical scheme for volatile organics analysis.

An internal standard of 1,4-dichlorobutane was added to 5 ml of the composited sample and the sample sparged with helium onto a Tenax GC-silica-packed sample tube. Two tubes were prepared, one for analysis and one duplicate. Tenax tubes were then sealed in glass under a nitrogen atmosphere and stored in a freezer at -18°C until analyzed.

Analyses were carried out using a Hewlett Packard 5981 GC-Mass Spectrometer with 5934 Data System. Sample tubes were heated to 180°C over a 1-minute period and held at that temperature for 4 minutes to desorb the compounds onto a Carbowax 1500 column held at -40°C. For compounds with boiling points below room temperature, cryogenic trapping at -40°C (liquid nitrogen cooling) was found to give better reproducibility of retention time than using the suggested temperature of 30°C. After desorption, the GC column temperature was raised 8°C/minute to 170°C.

Qualitative identification of a compound was made using three criteria listed in the protocol (1): 1) retention time must coincide with known retention times, 2) three characteristic masses must elute simultaneously, and 3) intensities of the characteristic masses must stand in the known proper proportions. Quantitation of volatile organics were made using response ratios to the 1,4-dichlorobutane internal standard.

Nonvolatile Organics

Nonvolatile organics are divided into three groups for analysis: base/neutral fraction, acid fraction (phenols), and pesticides and polychlorinated biphenyls (PCB). A list of compounds that are classified as nonvolatile organics is given in Appendix B. Due to the sources of wastewater in zinc manufacturing, pesticides were not analyzed in the samples.

The analytical procedure is described in Reference 1. Figure 5 depicts the sample processing scheme for the base/neutral and acid fractions. The sample solution, 2 ℓ, was made alkaline (pH greater than 11) with sodium hydroxide, and then extracted three times with methylene chloride. The wastewater samples formed emulsions upon extraction with methylene chloride. The problem was resolved by drawing off small amounts of separated solvent and pouring the extract through the sample in the separatory funnel. Separation was also enhanced by slowly dripping the emulsion onto the wall of a slightly tilted flask.

Extracts were dried on a column of anhydrous sodium sulfate, concentrated to 1.0 ml in a Kuderna-Danish (K-D) evaporator with a Snyder column spiked with deuterated anthracene, sealed in septum capped vials, and stored at 4°C until analysed. Analyses were performed on the GC-MS system using SP 2250 and Tenax GC columns for base/neutral and acid samples, respectively (1).

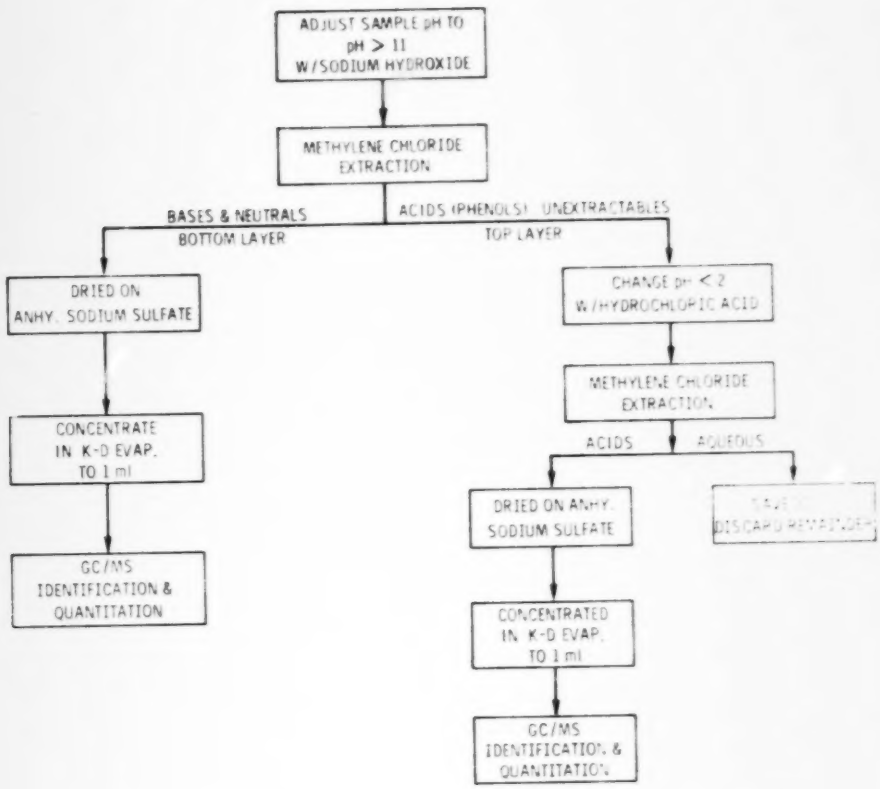

Figure 5. Sample processing scheme for non-volatile organics analysis.

Metals

In addition to the volatile and nonvolatile organics, the 129 chemical species include 13 metals, measured as the total metal. All metals were quantified by conventional flame and flameless atomic absorption techniques (3, 4).

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(3) Standard Methods for the Examination of Water and Wastewaters, Fourteenth Edition, American Public Health Association, Washington, D.C., 1976. 874 pp.

(4) Carter, M. J. and M. T. Huston Preservation of Phenolic Compounds in Wastewaters. Environmental Science and Technology, 12(3):309-313, 1978.

Five milliters of redistilled nitric acid were added to the metals samples in the laboratory and allowed to sit for two hours before removing aliquots for analysis. Due to the higher solids loading of the wastewater from the gas scrubber and lagoon wastestreams, this sample was vacuum filtered with 0.5 μm filters and both the filtrate and filter paper analyzed for metals.

The filter paper sample was parr bombed with nitric acid and the resulting solution diluted to 100 ml with distilled deionized water. Filter paper and reagent blanks were also prepared and analyzed.

The five sampling locations resulted in seven samples for metals analysis because two samples required filtration and analysis of filtrate and filter. Three of the sampled were split and analyzed as blind repeats. A certified National Bureau of Standards trace elements in water sample and two MRC standards, one in the 10 mg/l concentration range and one in the 0.05 mg/l range were used to calibrate the atomic absorption instrument. Two filter paper blanks, a nitric acid/water, and a distilled water blank were included in the analysis scheme.

Asbestos

Asbestos samples were collected at each of the five sampling points and preserved with a HgCl solution (1). Samples were then stored at 4°C for possible future analysis. No asbestos samples were analyzed for this project.

Cyanide (Total)

Total cyaniae was analyzed according to the procedure in Reference 1. One blind repeat and one spiked sample were included with the five samples for quality assurance.

Phenol (Total)

In addition to specific phenolic compounds and phenol measured by GC-MS, total phenol was also measured by typical wet chemistry techniques (1-3).

Phenol samples were preserved in the field by adding 1.0 g $CuSO_4$, maintaining the pH at less than 4 with H_3PO_4 and storing the sample at 4°C. Recent research has indicated this preservation technique is adequate for at least 8 days (4). All phenolic samples collected in this study were analyzed within 5 days of collection.

SECTION 5

RESULTS AND CONCLUSIONS

ORGANICS

The types and concentrations of organic priority pollutants found in the five water streams sampled are listed in Table 5. Five compounds in the effluent can be directly traced to the city water supply. These are methylene chloride, toluene, bis(2-ethyl hexyl)phthalate, bromodichloromethane and anthracene. Confirmation of the existence of these compounds in the city water supply from the city treatment plant is not possible at this time as no analysis by the city is available (samples have been taken by state authorities but data is not yet available). Trichlorofluoromethane in the effluent can be traced to the gas scrubber wastewater but is not added by the plant directly. The compound is either originating from the scrubbing operation on the roasting smoke stream or is forming at the scrubbing water temperature from chlorine in the water supply and flourine in the smoke stream. Trichloroethylene in the effluent can be traced to the scrubber wastewater, the holding lagoon, and the sanitary discharge. No trichloroethylene is used at the plant. Therefore, the compound is forming in these waste streams. Chlorine exists in cooling water going to the holding lagoon, city water going to the scrubber, and city water used for sanitary purposes. The compound is forming within the plant as it does not appear in plant intake water.

The phthalates found in all sample water streams can originate from the city water supply, as previously mentioned, PVC pipe used to transport the gas scrubber water and holding lagoon water to the treatment plant and gloves used during sampling in handling the wastewater. Fluoranthene in the lagoon water can also be traced to the city water supply although none was found in the effluent. Pyrene and benzo(a)pyrene found in the holding lagoon do not appear in the plant effluent.

The only compound in the plant discharge not appearing in any water stream going to the treatment plant is chloroform. As the plant does not chlorinate the effluent, this compound cannot be accounted for unless it exists in the slaked lime or flocculant added to the wastewater during precipitation/clarification.

TABLE 5. ORGANIC PRIORITY POLLUTANTS IN ZINC PLANT WATER STREAMS

Water source	Organic priority pollutant identified	Concentration, µg/ℓ
Plant intake (city water)	Methylene chloride	1.3
	Toluene	2.7
	Bromoform	5.3
	Dibromochloromethane	7.7
	Bromodichloromethane	9.3
	4-Chlorodiphenyl ether	2.4
	N-Nitrosodiphenylamine	4.6
	Bis(2-ethyl hexyl)phthalate	8.6
	Fluoranthene	5.4
	Benzo(a)anthracene	2.4
	Anthracene	0.1
Gas scrubber wastewater	Methylene chloride	224
	Toluene	57
	Trichlorofluoromethane	4.8
	Trichloroethylene	4.2
	Bis(2-ethyl hexyl)phthalate	22
Holding lagoon wastewater	Methylene chloride	3.3
	Toluene	8.0
	Trichloroethylene	2.6
	Diethyl phthalate	0.9
	Bis(2-ethyl hexyl)phthalate	8.7
	Anthracene	2.2
	Fluoranthene	2.2
	Pyrene	2.0
	Benzo(a)anthracene	1.2
Sanitary discharge	Methylene chloride	0.7
	Toluene	17
	Trichloroethylene	1.2
	Diethyl phthalate	3.6
	Bis(2-ethyl hexyl)phthalate	10
Plant effluent	Methylene chloride	2,610
	Toluene	8.8
	Trichlorofluoromethane	101
	Chloroform	53
	Bromodichloromethane	7.3
	Trichloroethylene	7.2
	Bis(2-ethyl hexyl)phthalate	107
	Anthracene	0.5

Analytical workup for organic priority pollutants involves the use of methylene chloride for extraction purposes. The high levels found in the gas scrubber waste stream and the plant effluent can be explained by possible contamination during analytical workup.

Collectively, except for the methylene chloride concentration in the plant effluent and scrubber wastewater, the levels equal or are less than 100 µg/ℓ. The majority are below 10 µg/ℓ. It should be emphasized that this analysis most importantly indicates the presence of the particular compound. Additional analysis is needed to more accurately quantify the actual concentrations. No mass loadings or effluent factors were calculated for these organics.

Finally, it should also be emphasized that none of the compounds identified is directly added by the plant. Compounds identified are either being formed chemically within the plant, being picked up as stream contaminants from pumps, pipes, or quench operations, or coming to the plant in the city water supply.

Metals

Priority pollutant metals found in the five sample locations are presented in Table 6. Mass loadings into and out of the treatment plant with removal efficiencies are shown in Table 7. It should be noted that with solids overflow from the thickener re-entering the lagoon, metals concentrations are higher than if no recycle was occurring. Thus, mass loadings for the lagoon are higher than the true loadings originating from plant wastewaters. Each individual waste stream entering the lagoon would have to be measured to get actual mass loadings for plant wastewater going to the treatment system. Metals removal is in general quite good for this treatment plant. This fact is expected for the amount of lime being added and the pH of the discharge. By keeping the pH high, metals are remaining insoluble and thus increasing removal efficiency.

Metal effluent factors for the sampled waste streams and plant effluent are given in Table 8. In addition, effluent factors for the gas scrubber waste stream based on H_2SO_4 production are given in Table 9.

Net metal effluent factors are given in Table 10. These factors account for metal concentrations not added by the plant but present in the incoming city water supply. Production figures and water usage rates used as a basis for calculations are presented in Appendix C.

TABLE 6. METALS ANALYSIS - AA

Metal (total)	Gas scrubber liquid, mg/l	Gas scrubber solids		Lagoon liquid, mg/l	Lagoon solids		Sanitary, mg/l	City water, mg/l	Effluent, mg/l
		mg/g	mg/l		mg/g	mg/l			
Silver	0.01	11	0.73	0.09	0.62	0.11	0.01	<0.01	0.02
Beryllium	<0.02	<0.10	<0.01	<0.02	<0.04	<0.01	<0.01	<0.01	<0.01
Cadmium	42	12	0.83	8.1	2.9	0.51	7.0	<0.01	0.02
Chromium	0.11	0.11	<0.007	2.2	<0.04	<0.01	<0.01	<0.01	0.14
Copper	24	4.5	0.31	6.2	2.1	0.44	0.69	0.02	0.03
Nickel	0.01	0.05	0.04	0.08	<0.02	<0.01	<0.01	<0.01	<0.01
Lead	17	210	15	8.5	26	4.4	0.57	<0.05	<0.05
Antimony	<1.5	<8.4	<0.59	<1.5	<3.0	<0.52	<0.8	<0.8	<0.8
Zinc	78	60	4.1	2,100	36	6.2	110	0.38	1.1
Arsenic	<2.6	<0.11	<0.01	0.84	0.45	0.08	0.05	<0.01	<0.01
Mercury	<0.01	11	1.00	0.02	0.65	0.11	<0.02	<0.01	<0.01
Thallium	0.32	<0.53	<0.04	<0.09	<0.19	<0.03	<0.05	<0.05	<0.05
Selenium	0.35	12	0.83	0.17	0.09	0.01	<0.01	<0.01	<0.04

TABLE 7. METAL MASS LOADINGS AND REMOVAL EFFICIENCIES FOR WASTE TREATMENT PLANT (AA BASIS)

Metal (total)	Gas scrubber liquid, kg/day	Gas scrubber solids, kg/day	Lagoon liquid, kg/day	Lagoon solids, kg/day	Plant effluent, kg/day	Removal efficiency, percent
Silver	0.003	0.18	0.25	0.29	0.04	94
Beryllium	<0.005	<0.002	<0.05	<0.02	<0.3	-[a]
Cadmium	10	0.20	21	1.3	0.06	100
Chromium	0.027	0.002	5.8	<0.02	0.41	93
Copper	6.00	0.08	16	1.2	0.10	100
Nickel	0.002	0.009	0.21	<0.001	<0.01	94
Lead	4.07	3.5	22	12	<0.14	100
Antimony	<0.37	<0.14	<4.0	<1.4	<2.3	-[a]
Zinc	19	1.0	5,500	17	3.3	100
Arsenic	0.64	<0.002	2.2	0.21	<0.03	99
Mercury	0.001	0.24	0.04	0.30	<0.006	99
Thallium	0.08	<0.01	<0.24	<0.09	<0.14	-[a]
Selenium	0.08	0.20	0.45	0.04	0.12	85

[a]Removal efficiency cannot be calculated since the metal concentration in all samples was below instrument detection limits.

TABLE 8. METAL EFFLUENT FACTORS FOR SAMPLED ZINC PLANT (AA BASIS)

Metal (total)	Effluent factor, mg/kg of cathode zinc				
	Gas scrubber liquid	Gas scrubber solids	Lagoon liquid	Lagoon solids	Plant effluent
Silver	0.02	0.95	1.3	1.5	0.23
Beryllium	<0.03	<0.01	<0.28	<0.08	<0.15
Cadmium	54	1.07	113	7.1	0.34
Chromium	0.14	0.01	31	<0.09	2.2
Copper	32	0.40	87	6.1	0.53
Nickel	0.01	0.05	1.1	<0.01	<0.07
Lead	21	19	119	62	<0.74
Antimony	<2.0	<0.74	<21	<7.30	<12
Zinc	100	5.3	29,000	88	17
Arsenic	3.4	<0.01	12	1.1	<0.15
Mercury	0.005	1.3	0.24	0.06	<0.03
Thallium	0.41	<0.05	<1.3	<0.45	<0.77
Selenium	0.45	1.1	2.4	0.21	0.61

TABLE 9. METAL EFFLUENT FACTORS FOR SAMPLED ZINC PLANT (GAS SCRUBBER/H_2SO_4)

Metal	Effluent factor, mg/kg of H_2SO_4	
	Atomic adsorption basis (AA)	
	Gas scrubber liquid	Gas scrubber solids
Silver	0.02	1.1
Beryllium	<0.03	<0.01
Cadmium	63	1.2
Chromium	0.16	0.01
Copper	36	0.47
Nickel	0.01	0.05
Lead	25	22
Antimony	<2.3	<0.86
Zinc	117	6.2
Arsenic	3.9	<0.01
Mercury	0.01	1.5
Thallium	0.48	<0.06
Selenium	0.53	1.2

TABLE 10. NET METAL MASS EFFLUENT FACTORS FOR SAMPLED ZINC PLANT

Metal (total) (AA)	Net effluent factor, mg/kg of product		
	Plant effluent	City water supply	Net effluent factor
Silver	0.23	0.13	0.10
Beryllium	<0.15	<0.21	-[a]
Cadmium	0.34	<0.10	0.29 ± 0.05
Chromium	2.17	<0.20	2.1 ± 0.1
Copper	0.53	0.39	0.14
Nickel	<0.07	<0.10	-[a]
Lead	<0.74	<1.02	-[a]
Antimony	<12	<12	-[a]
Zinc	17	5.8	11
Arsenic	<0.15	<0.20	-[a]
Mercury	<0.03	<0.04	-[a]
Thallium	<0.77	<1.0	-[a]
Selenium	0.61	<0.02	0.6 ± 0.01

[a]Net effluent factor cannot be calculated since the metal concentration in both samples was below instrument detection limits.

These data show the treatmhnt plant to be effectively reducing all metals added to city water during plant use to acceptable and applicable state discharge requirement levels.

Flow, pH, Temperature

Temperature and pH measurements taken during the sampling period for the plant effluent are shown in Table 11. Additional pH measurements and flow measurements are presented in Appendix C.

TABLE 11. DATA COLLECTED FOR PLANT DISCHARGE

Sampling Point: Plant Discharge
Sampling Period: 10:00 A.M. March 8, 1978 to
10:00 A.M. March 10, 1978

Hour	Temperature, °F	pH
3/8/78		
10	64	10.3
11	64	10.3
12	64	10.3
1	64	10.3
2	64	10.3
3	65	10.1
4	65	10.1
5	64	10.0
6	64	10.0
7	64	10.0
8	65	9.9
9	65	9.9
10	64	9.9
11	64	10.0
12	64	9.9
3/9/78		
1	64	9.8
2	64	9.9
3	64	9.9
4	63	9.9
5	63	9.9
6	62	9.9
7	60	9.9
8	62	9.9
9	64	9.8
10	64	9.9
11	65	9.9
12	66	9.9
1	66	9.9
2	67	9.9
3	67	9.9
4	67	9.9
5	68	9.8
6	68	9.9
7	69	9.8
8	69	9.8
9	70	9.8
10	70	9.7
11	71	9.7
12	72	9.7
3/10/78		
1	71	9.7
2	71	9.7
3	71	9.7
4	71	9.7
5	71	9.6
6	71	9.7
7	71	9.6
8	72	9.6
9	73	9.6

Total Phenol and Total Cyanide

Cyanide concentrations in all samples were below the detection limit of .002 mg/l. Phenol concentrations in all samples were below the detection limit of .002 mg/l except for the sanitary discharge. This point had a phenol concentration of .007 mg/l.

Waste Treatment System

The waste treatment system at the sampled plant utilized the best design parameters available as originally conceived. However, as currently operated, the plant is less than 100 percent efficient.

During the sampling period, the plant was experiencing a solids overloading of both the reactor clarifier and the sludge thickener. During the sampling period no more than a 0.9 meter clear depth in the reactor clarifier was observed and intermittent overflow of solids from the sludge thickener back to the holding lagoon was a common occurrence. The treatment system was originally designed to have the clear overflow from the thickener discharged to the flash mixing tank. Due to the solids overloading, this overflow is now returned to the holding lagoon. The lagoon was not designed to handle any solids and thus two undesigned operating conditions currently exist. First, the lagoon has over a period of time accumulated solids from the sludge thickener overflow so that a majority of the holding lagoon capacity has been lost. Second, a dredge has been placed in the lagoon to pump solids back to the treatment plant for settling and removal. However, this operation has strained the system even further. In short, the treatment plant is producing more solids than the thickener/vacuum filter can remove. Solids are simply being recycled within the treatment system and the lagoon.

By increasing vacuum filter capacity, this problem could potentially be reduced.

A water balance of this treatment plant (with current design modifications) is presented in Appendix C.

SECTION 6

REFERENCES

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2. Manual of Methods for Chemical Analysis of Water and Wastes. EPA-625/6-76-003a (PB 259 973). U.S. Environmental Protection Agency, Cincinnati, Ohio, 1976. 317 pp.

3. Standard Methods for the Examination of Water and Wastewaters, Fourteenth Edition, American Public Health Association, Washington, D.C., 1976. 874 pp.

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5. Standard for Metric Practice. ANSI/ASTM Designation: E 380-76$^{\epsilon}$, IEEE Std. 268-1976, American Society for Testing and Materials, Philadelphia, Pennsylvania, February 1976. 37 pp.

APPENDIX A

RECOMMENDED LIST OF PRIORITY POLLUTANTS

TABLE A-1. RECOMMENDED LIST OF PRIORITY POLLUTANTS

Compound name
Acenaphthene
Acrolein
Acrylonitrile
Benzene
Benzidine
Carbon tetrachloride (tetrachloromethane)
Chlorinated benzenes (other than dichlorobenzenes)
Chlorobenzene
1,2,4-Trichlorobenzene
Hexachlorobenzene
Chlorinated ethanes (including 1,2-dichloroethane, 1,1,1-trichloroethane and hexachloroethane)
1,2-Dichloroethane
1,1,1-Trichloroethane
Hexachloroethane
1,1-Dichloroethane
1,1,2-Trichloroethane
1,1,2,2-Tetrachloroethane
Chloroethane
Chloroalkyl ethers (chloromethyl, chloroethyl and mixed ethers)
Bis(chloromethyl) ether
Bis(2-chloroethyl) ether
2-Chloroethyl vinyl ether (mixed)
Chlorinated naphthalene
2-Chloronaphthalene

(continued)

TABLE A-1 (continued).

Compound name
Chlorinated phenols (other than those listed elsewhere; includes trichlorophenols and chlorinated cresols)
2,4,6-Trichlorophenol
p-Chloro-*m*-cresol (4-chloro-3-methylphenol)
Chloroform (trichloromethane)
2-Chlorophenol
Dichlorobenzenes
1,2-Dichlorobenzene
1,3-Dichlorobenzene
1,4-Dichlorobenzene
Dichlorobenzidine
3,3'-Dichlorobenzidine
Dichloroethylenes (1,1-dichloroethylene and 1,2-dichloroethylene)
1,1-Dichloroethylene (vinylidine chloride)
1,2-*Trans*-dichloroethylene
2,4-Dichlorophenol
Dichloropropane and dichloropropene
1,2-Dichloropropane
1,3-Dichloropropylene (*cis* and *trans*-1,3-dichloropropene)
2,4-Dimethylphenol
Dinitrotoluene
2,4-Dinitrotoluene
2,6-Dinitrotoluene
1,2-Diphenylhydrazine
Ethylbenzene
Fluoranthene

(continued)

TABLE A-1 (continued).

Compound name
Haloethers (other than those listed elsewhere)
4-Chlorophenyl phenyl ether
4-Bromophenyl phenyl ether
Bis(2-chloroisopropyl) ether
Bis(2-chloroethoxy) methane
Halomethanes (other than those listed elsewhere)
Methylene chloride (dichloromethane)
Methyl chloride (chloromethane)
Methyl bromide (bromomethane)
Bromoform (tribromomethane)
Dichlorobromomethane
Trichlorofluoromethane
Dichlorodifluoromethane
Chlorodibromomethane
Hexachlorobutadiene
Hexachlorocyclopentadiene
Isophorone (3,5,5-trimethyl-2-cyclohexen-1-one)
Naphthalene
Nitrobenzene
Nitrophenols (including 2,4-dinitrophenol and dinitrocresol)
2-Nitrophenol
4-Nitrophenol
2,4-Dinitrophenol
4,6-Dinitro-o-cresol
Nitrosoamines
N-nitrosodimethylamine
N-nitrosodiphenylamine
N-nitroso-di-n-propylamine
Penta chlorophenol
Phenol

(continued)

TABLE A-1 (continued).

Compound name
Phthalate esters
Bis(2-ethylhexyl) phthalate
Butyl benzyl phthalate
Di-n-butyl phthalate
Diethyl phthalate
Dimethyl phthalate
Di-n-octyl phthalate
Polynuclear aromatic hydrocarbons
Benz(a)anthracene (1,2-benzanthracene)
Benzo(a)pyrene (3,4-benzopyrene)
3,4-Benzofluoranthene
Benzo(k)fluoranthene (11,12-benzofluoranthene)
Chrysene
Acenaphthylene
Anthracene
Benzo(ghi)perylene (1,12-benzoperylene)
Fluorene
Phenanthrene
Dibenz(ah)anthracene (1,2,5,6-dibenzanthracene)
Indeno(1,2,3-cd)pyrene (2,3-o-phenylenepyrene)
Pyrene
Tetrachloroethylene
Toluene
Trichloroethylene
Vinyl chloride (chloroethylene)
Pesticides and metabolites
Aldrin
Dieldrin
Chlorodane (technical mixture and metabolites)
DDT and metabolites
4,4'-DDT
4,4'-DDE (p,p'-DDX)
4,4'-DDD (p,p'-TDE)

(continued)

TABLE A-1 (continued).

Compound name
Endosulfan and metabolites
α-Endosulfan
β-Endosulfan
Endosulfan sulfate
Endrin and metabolites
Endrin
Endrin aldehyde
Heptachlor and metabolites
Heptachlor
Heptachlor epoxide
Hexachlorocyclohexane
α-BHC
β-BHC
λ-BHC (lindane)
δ-BHC
Polychlorinated biphenyls (PCB)
PCB-1242 (Arochlor 1242)
PCB-1254 (Arochlor 1254)
PCB-1221 (Arochlor 1221)
PCB-1232 (Arochlor 1232)
PCB-1248 (Arochlor 1248)
PCB-1260 (Arochlor 1260)
PCB-1016 (Arochlor 1016)
Toxaphene
Elements
Antimony (Total)
Arsenic (Total)
Asbestos (Fibrous)
Beryllium (Total)
Cadmium (Total)
Chromium (Total)
Copper (Total)
Cyanide (Total)
Lead (Total)

(continued)

TABLE A-1 (continued).

Compound name
Elements (continued)
Mercury (Total)
Nickel (Total)
Selenium (Total)
Silver (Total)
Thallium (Total)
Zinc (Total)
2,3,7,8-Tetrachlorodibenzo-*p*-dioxin (TCDD)

APPENDIX B

PRIORITY POLLUTANT ANALYSIS FRACTIONS

TABLE B-1. VOLATILE COMPOUNDS

Compound	Compound
Chloromethane	1,2-Dichloropropane
Dichlorodifluoromethane	*trans*-1,3-dichloropropene
Bromomethane	Trichloroethylene
Vinyl chloride	Dibromochloromethane
Chloroethane	*Cis*-1,3-dichloropropene
Methylene chloride	1,1,2-Trichloroethane
Trichlorofluoromethane	Benzene
1,1,-Dichloroethylene	2-Chloroethyl vinyl ether
1,1-Dichloroethane	Bromoform
trans-1,2,-dichloroethane	1,1,2,2-Tetrachloroethylene
Chloroform	1,1,2,2-Tetrachloroethane
1,2-Dichloroethane	Toluene
1,1,1-Trichloroethane	Chlorobenzene
Carbon tetrachloride	Ethylbenzene
Bromodichloromethane	Acrolein
Bis(chloromethyl) ether	Acrylonitrile

TABLE B-2. BASE NEUTRAL EXTRACTABLE COMPOUNDS

Compound	Compound
1,3-Dichlorobenzene	Anthracene
1,4-Dichlorobenzene	Diethyl phthalate
Hexachloroethane	Dimethyl phthalate
1,2-Dichlorobenzene	Fluoranthene
Bis(2-chloroisopropyl) ether	Pyrene
Hexachlorobutadiene	Di-n-butyl phthalate
1,2,4-Trichlorobenzene	Benzidine
Naphthalene	Butyl benzyl phthalate
Bis(2-chloroethyl) ether	Chrysene
Hexachlorocyclopentadiene	Bis(2-ethylhexyl) phthalate
Nitrobenzene	Benz(a)anthracene
Bis(2-chloroethoxy) methane	Benzo(b)fluoranthene
2-Chloronaphthalene	Benzo(k)fluoranthene
Acenaphthylene	Benzo(a)pyrene
Acenaphthene	Indeno(1,2,3-cd)pyrene
Isophorone	Dibenz(a,h)anthracene
Fluorene	Benzo(g,h,i)perylene
2,6-Dinitrotoluene	N-nitrosodimethylamine
1,2-Diphenylhydrazine	N-nitroso-di-n-propylamine
2,4-Dinitrotoluene	4-Chlorophenyl phenyl ether
N-nitrosodiphenylamine	3,3'-Dichlorobenzidine
Hexachlorobenzene	2,3,7,8-Tetrachlorodibenzo-*p*-dioxin[a]
4-Bromophenyl phenyl ether	Bis-(chloromethyl) ether
Phenanthrene	

[a]This compound was specifically listed in the consent decree. Because of TCDD's extreme toxicity, EPA recommends that laboratories not acquire analytical standards for this compound.

TABLE B-3. ACID EXTRACTABLE COMPOUNDS

2-Chlorophenol
Phenol
2,4-Dichlorophenol
2-Nitrophenol
p-Chloro-*m*-cresol
2,4,6-Trichlorophenol
2,4-Dimethylphenol
2,4-Dinitrophenol
4,6-Dinitro-*o*-cresol
4-Nitrophenol
Pentachlorophenol

TABLE B-4. PESTICIDES AND PCB

Compound
β-Endosulfan
α-BHC
γ-BHC
β-BHC
Aldrin
Heptachlor
Heptachlor epoxide
α-Endosulfan
Dieldrin
4,4'-DDE
4,4'-DDD
4,4'-DDT
Endrin
Endosulfan sulfate
δ-BHC
Chlordane
Toxaphene
PCB-1242 (Aroclor 1242)
PCB-1254 (Aroclor 1254)
PCB-1221 (Aroclor 1221)
PCB-1232 (Aroclor 1232)
PCB-1248 (Aroclor 1248)
PCB-1260 (Aroclor 1260)
PCB-1016 (Aroclor 1016)

TABLE B-5. METALS AND OTHER COMPOUNDS

Metals, total	Others
Antimony	Asbestos
Arsenic	Cyanide
Beryllium	
Cadmium	
Chromium	
Copper	
Lead	
Mercury	
Nickel	
Selenium	
Silver	
Thallium	
Zinc	

APPENDIX C

PLANT PRODUCTION AND TREATMENT PLANT DATA

Table C-1 presents data taken by the treatment plant operators during sampling. The data is in English units. Table C-2 is plant production data for 1977. Figure C-1 is a water balance of the waste treatment plant.

TABLE C-1. LOG SHEET WASTEWATER TREATING UNIT

	8:00 AM	10:00 AM	12:00 AM	2:00 PM	4:00 PM	6:00 PM	8:00 PM	10:00 PM	12:00 PM	2:00 AM	4:00 AM	6:00 AM
Effluent flow (gal/day)	937,500	850,000	575,000	837,500	837,500	926,250	1,225,000	1,275,000	750,000	750,000	987,500	887,500
Effluent pH	10.2	10.3	10.2	10.1	10.1	10.0	10.0	9.9	9.9	9.9	9.9	9.9
Effluent temperature, °F	65°	64°	64°	65°	65°	64°	64°	65°	64°	64°	63°	63°
Effluent suspended solids	0	0	0	0	0	0	0	0	0	0	0	0
Reactor well pH	8.06	10.3	9.65	10.0	9.63	10.30	8.5	9.65	8.6	10.4	9.0	9.6
Reactor meter pH	8.3	10.8	9.8	10.4	6.7	10.4	9.8	10.0	8.9	10.5	9.0	10.2
Neutralization pH	-	-	-	-	-	-	-	-	-	-	-	-
Lime feed manual/ automatic	Auto.	Auto.	Auto.	Auto.	Auto.	Auto.	Auto.	Auto.	Auto.	Auto.	Auto.	Auto.
Lime feed rate	8/100	8/100	8/100	8/100	8/100	8/100	8/100	8/100	8/100	8/100	8/100	8/100
Lime slaker water rate	4,820	Off	4,820	Off	4,820	Off	4,820	4,820	Off	Off	4,820	Off
SO_2 scrubber water flow (gpm)	30	30	30	30	24	24	24	24	24	24	24	24
SO_2 scrubber water pH	1.2	1.3	1.3	1.35	1.38	1.32	1.20	1.04	1.2	1.3	1.2	1.2
Lagoon water pH	2.4	2.54	2.6	2.36	2.2	1.84	1.32	2.24	1.9	2.0	2.2	2.1
Reactor well % solids	85	85	85	80	84	82	82	82	84	85	84	84
R-C mid-level % solids	88	88	90	85	80	86	86	88	90	90	92	92
Clear depth clarifier, ft.	3	2	1-1/2	1-3/4	1-1/8	3	2	4	1-3/4	3	3-1/2	3-1/2
3 in. Denver mud pump	On	On	On	On	On	On	On	On	On	On	On	On
Filter on/off	On	On	On	On	On	On	On	On	On	On	On	On
G-D mud pump on/off	On	On	On	On	On	On	On	On	On	On	On	On
600 gpm on/off	On	On	On	On	On	On	On	On	On	On	On	On
500 gpm on/off	Off	Off	Off	Off	Off	Off	Off	Off	Off	Off	Off	Off

(continued)

TABLE C-1 (continued).

	8:00 AM	10:00 AM	12:00 AM	2:00 PM	4:00 PM	6:00 PM	8:00 PM	10:00 PM	12:00 PM	2:00 AM	4:00 AM	6:00 AM
Effluent flow (gal/day)	962,500	800,000	950,000	900,000	375,000	825,000	650,000	537,500	525,000	487,500	475,000	450,000
Effluent pH	9.9	9.9	9.9	9.8	9.9	9.8	9.8	9.7	9.7	9.7	9.7	9.6
Effluent temperature, °F	62°	64°	64°	66°	67°	68°	69°	70°	71°	71°	71°	71°
Effluent suspended solids	0	0	0	0	0	0	0	0	0	0	0	0
Reactor well pH	8.2	11.32	8.5	9.5	9.6	9.6	9.9	10.4	9.9	11.0	7.9	10.0
Reactor meter pH	8.4	11.6	8.0	9.5	9.9	9.4	10.3	10.7	10.0	11.5	8.2	10.5
Neutralization pH	-	-	-	-	-	-	-	-	-	-	-	-
Lime feed manual/ automatic	Auto.	Auto.	Auto.	Auto.	Auto.	Auto.	Auto.	Auto.	Auto.	Auto.	Auto.	Auto.
Lime feed rate	8/100	8/100	8/100	8/100	8/100	8/100	8/100	8/100	8/100	8/100	8/100	8/100
Lime slaker water rate	4,820	Off	4,820	4,820	Off	4,820	Off	Off	Off	Off	4,820	Off
SO_2 scrubber water flow (gpm)	24	24	24	24	20	0	10	10	0	20	20	0
SO_2 scrubber water pH	1.50	1.60	1.52	1.5	1.4	-	1.1	1.0	-	1.1	1.2	-
Lagoon water pH	1.6	9.53	6.76	6.47	6.5	6.5	9.9	7.6	2.8	3.0	2.8	2.7
Reactor well % solids	70	85	90	92	92	88	87	80	82	95	89	90
R-C mid-level % solids	80	85	94	92	94	85	90	81	90	90	95	95
Clear depth clarifier, ft	3-3/4	4	4	3-3/4	5	2-1/2	2	1-1/2	2	2	2	2
3 in. Denver mud pump	On	Off	Off	Off	On	Off	On	On	On	On	On	On
Filter on/off	On	On	On	On	On	Off	On	On	On	On	On	Off
G-D mud pump on/off	On	On	On	On	Off	Off	On	On	On	On	On	Off
600 gpm on/off	On	Off	Off	Off	Off	Off	Off	Off	On	On	On	On
500 gpm on/off	Off	Off	Off	Off	Off	Off	Off	Off	Off	Off	Off	Off

TABLE C-2. PRODUCTION FIGURES FOR SAMPLED PLANT (1977)

Total production	
Cathode zinc:	69,008 metric tons
Cathode cadmium:	218 metric tons
H_2SO_4 production:	59,474 metric tons (98% H_2SO_4)
Water usage	
City water:	1,406,377 kiloliters
City water demineralized:	506,293 kiloliters
Water treated from gas scrubber water:	98,410 kiloliters
Water treated from holding lagoon:	828,915 kiloliters
Total water treated:	927,325 kiloliters
Dry residue from treatment plant:	2,906 metric tons at 20% by volume solids

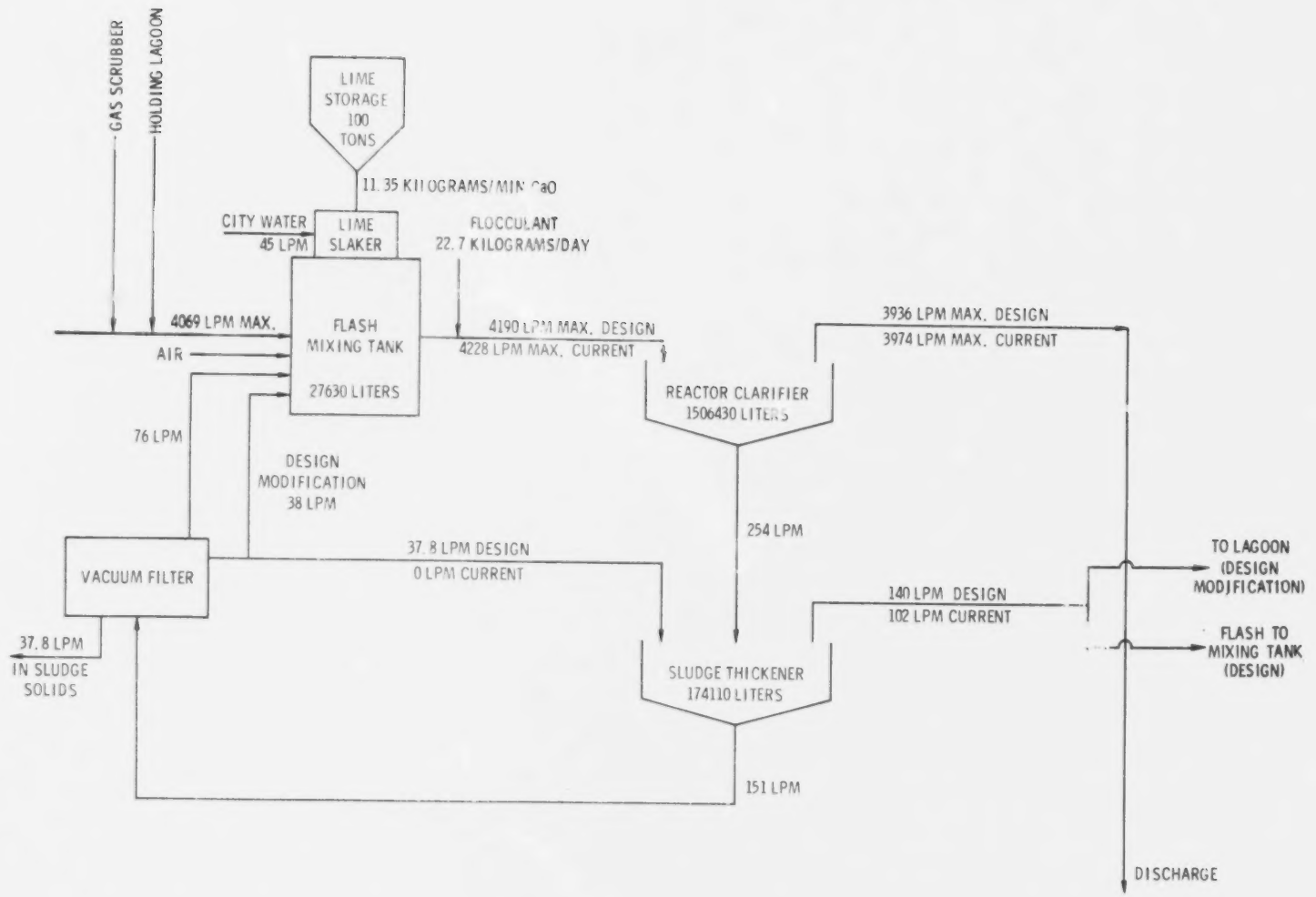

Figure C-1. Water balance for treatment plant design and current operation.

CONVERSION FACTORS AND METRIC PREFIXES (5)

CONVERSION FACTORS

To convert from	To	Multiply by
Degree Celsius (°C)	Degree Fahrenheit (°F)	$t°_F = 1.8\ t°_C + 32$
Kilogram (kg)	Pound-mass (avoirdupois)	2.205
Liter/s (ℓ/s)	Gallon (U.S. liquid)/min (gpm)	1.585×10^1
Meters^3/s (m^3/s)	Foot^3/min (cfm)	2.119×10^3

METRIC PREFIXES

Prefix	Symbol	Multiplication factor	Example
Kilo	k	10^3	5 kg = 5×10^3 grams
Milli	m	10^{-3}	5 mg = 5×10^{-3} gram
Micro	μ	10^{-6}	5 mg = 5×10^{-3} gram

(5) Standard for Metric Practice. ANSI/ASTM Designation: E 380-76$^{\varepsilon}$, IEEE Std. 268-1976, American Society for Testing and Materials, Philadelphia, Pennsylvania, February 1976. 37 pp.